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(71) Applicant (for all designated States except US): UWS
VENTURES LIMITED [GB/GB]; University of Wales,
Singleton Park, Swansea SA2 8PP (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): WORSLEY, David,
Anthony [GB/GB]; Ffynnon Gro, Llanfynydd, Car-
marthen SA32 7TO (GB). MCMURRAY, Hamilton, Neil
[GB/GB]; 10 Heol Gwrysydd, Treboeth, Swansea SA5
9HN (GB).

(74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield,
Nr Westerham, Kent TN16 2BB (GB).

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(54) Title: ANTI-CORROSION PIGMENTS

(57) Abstract: Corrosion inhibitor pigments consisting of nitrate, carbonate and chromate (VI) - exchanged hydrotalcite are effective for the inhibition of filiform corrosion (ffc) on coated AA2024-T3 aluminum alloy samples.

Anti-corrosion Pigments

The present invention relates to anti-corrosion pigments based on clays.

- 5 Chromate (VI) based anti-corrosion pigments are widely used in primer systems for the protection of aluminium surfaces. However, the well-documented toxic and carcinogenic nature of Cr(VI) means that there is a requirement for effective, environmentally friendly alternatives. Considerable research is presently underway to elucidate the pathways by which water soluble Cr(VI)-oxo species inhibit corrosion
- 10 activity on precipitation hardened aluminium aerospace alloys such as AA2024-T3, in order that other inhibitors exhibiting some, if not all, of the attributes of CrO_4^{2-} can be developed.

- 15 It has been demonstrated that cation exchange pigments based on naturally occurring bentonite clay can efficiently inhibit corrosion driven delamination on galvanised steel surfaces. The bentonite ion exchange matrix provides a delivery system for inhibitor ions such as rare earth or alkali earth metal cations, which are only released when electrolyte is encountered on a corroding metal surface.

- 20 We have now found that an anionic clay can be used to generate anti-corrosion pigments capable of delivering anionic inhibitor species onto corroding metal surfaces.

- 25 According to the invention there is provided an exchangeable anion-bearing hydrotalcite powder as an anti-corrosion pigment.

The invention also comprises anti-corrosion formulations containing an exchangeable anion-bearing hydrotalcite.

- 30 The invention also comprises protective coatings incorporating an exchangeable

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anion-bearing hydrotalcite powder as an anti-corrosion pigment.

Hydrotalcite type compounds refer to synthetic lamellar mixed hydroxides represented by the general formula $[M2^{2+}_{1-x} M3^{3+}_x(OH)_2]^{x+} [A^{x-} \cdot nH_2O]$, where M2 is a divalent metal, M3 is a trivalent metal and A is an anion.

The hydrotalcites (HTs) have a layer-type structure similar to brucite ($Mg(OH)_2$). Isomorphous substitution of divalent metal ions (e.g. Mg^{2+}) with cations of higher charge (such as Al^{3+}) results in positively charged layers. Electroneutrality is preserved by anions (typically carbonate) located within the hydrated interlayer regions.

Any metal with the appropriate valency and suitable properties can be used and the preferred metal M2 is magnesium and the preferred metal M3 is aluminium.

Hydrotalcite materials have widespread use in the field of catalysis. Recent developments in HT based catalysts for a range of organic and inorganic reactions are comprehensively reviewed by Vaccari the reference below.

It is well known that hydrotalcite and hydrotalcite like compounds (HTLs) will decompose in a predictable manner upon heating and that, if the heating does not exceed certain temperatures, the resulting decomposed materials can be rehydrated (and, optionally, resupplied with various anions, e.g., CO_3^{2-} , that were driven off by the heating process) and thereby reproduce the original, or a very similar, HTL compound. The decomposition products of such heating are often referred to as "collapsed," or "metastable," hydrotalcite-like compounds. If, however, these collapsed or metastable materials are heated beyond certain temperatures (e.g., $900^\circ C$); then the resulting decomposition products of such hydrotalcite-like compounds can no longer be rehydrated and, hence, are no longer capable of forming the original hydrotalcite-like compound.

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Such thermal decomposition of hydrotalcite-like compounds has been carefully studied and fully described in the academic and patent literature. For example, Miyata, "Physico-Chemical Properties of Synthetic Hydrotalcites in Relation to Composition," Clays and Clay Minerals, Vol. 28, No. 1, 50-56 (1980), describes the temperature relationships and chemical identity of the thermal decomposition products of hydrotalcite in the face of a rising temperature regime.

HTs containing these anions are referred to as exchangeable anion-bearing HTs.

10 The HT matrix can be used as a generic support material for a wide range of potential inhibitor anions, which has the added benefit of enabling the performance of such species to be compared under identical conditions; this enables the HT anion-bearing pigment to be significantly more versatile than existing pigment technologies based on sparingly soluble salts. Any suitable anion can be used; the preferred anions are
15 anions with corrosion inhibitor properties, oxidising agents or bases and preferably are capable of becoming strongly adsorbed at metal surfaces and (hydr)oxide covered metal surfaces and are capable of forming sparingly soluble precipitates with metal cations.

20 Preferred anions include a transition metal oxyanion, a group (III) oxyanion, a group (IV) oxyanion, a group (V) oxyanion, a group (VI) oxyanion, or a group (VII) oxyanion e.g. nitrate (NO_3^-), nitrite (NO_2^-), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}) bicarbonate (HCO_3^-), molybdate (MoO_4^{2-}) permanganate (MnO_4^{2-}).

25

The anti-corrosion pigments can be made from commercially available hydrotalcite (HT) powder by a process comprising an initial heat treatment stage, followed by re-hydration in an aqueous inhibitor anion solution to produce the anion exchange anti-corrosion pigment. The hydrotalcite clays which can be used as the anion exchange

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matrix include commercially available magnesium aluminium hydroxy-carbonate powders.

5 Preferably the hydrotalcite clay is calcined (heated in air) to temperatures between 200°C and 600°C to produce an amorphous mixture of metal hydroxides. The amorphous mixture of hydroxides is then cooled to room temperature and rehydrated using an aqueous solution containing the desired exchangeable anion. It is thought that the rehydration acts to restore the lamella structure, generating positively charged magnesium-aluminium hydroxide (Brucite) layers with the exchangeable anion in the
10 interlayer spaces.

The pigments of the present invention can be used in a suitable carrier to form an anti-corrosion surface coating such as a primer or paint to cover the surface to be treated. Any of the typically used carriers can be used depending on the application.
15 Preferably the composition is applied as a film and such films can be formed based on resins or polymers such as polyvinyl butyral (PVB) films, tall-oil modified polyester solutions etc.

It is a feature of the present invention that the HT based anion exchange pigments can
20 provide an effective delivery system for dispensing inhibitor anions on corroding aluminium surfaces and each hydrotalcite-based pigment can produce a profound inhibition of filiform corrosion (ffc) attack when compared to control samples coated with un-pigmented PVB.

25 The invention is illustrated in the examples.

Examples

Model systems consisting of non-pretreated AA2024-T3 aluminium alloy substrates
30 coated with polyvinyl butyral (PVB) films, in which fixed volume fractions of HT

based pigments are dispersed, were tested. Following initiation by applying aqueous HCl onto a penetrative coating, the performance of inhibitor pigments dispersed in polyvinyl butyral (PVB) films was quantified by means of repeated in-situ scanning of a fixed sample area using a scanning Kelvin microprobe apparatus. The preparation is shown schematically in the drawings together with results.

Referring to the drawings:

Figure 1 is a schematic illustration showing the two stages of HT pigment preparation along with the structural transformations involved.

Figure 2 is a schematic diagram showing (a) sample preparation and (b) experimental procedure.

Figure 3 shows (a) the quantity of CrO_4^{2-} released from CrO_4^{2-} exchanged calcined HT, on dispersing 1g of HT in 100ml of 0.1M aqueous solutions of $\text{Na}_2\text{CO}_3^{2-}$, NaOH and NaCl and (b) the quantity of CrO_4^{2-} released from 1g of CrO_4^{2-} exchanged calcined HT following successive re-dispersions in 100 ml aliquots of 0.1 M aqueous Na_2CO_3 .

Figure 4 is photographic images showing 1cm^2 areas surrounding a penetrative scribe on PVB coated AA2024-T3 aluminium alloy samples after a period of 7 days following ffc initiation using aqueous HCl, when maintained at a constant relative humidity of 93%. The appearance of a sample coated using un-pigmented PVB is shown in (a), while samples coated with carbonate, nitrate and chromate exchanged HT-containing films at a pigment volume fraction (ϕ) of 0.2 are given in (b), (c) and (d) respectively.

Figure 5 shows the quantification of the average corroded sample area for AA2024-T3 samples coated using HT pigmented and un-pigmented PVB films after a period of 7 days following ffc initiation.

Figure 6 shows FFC delaminated area, quantified by repetitive scanning of a fixed sample area by means of a SKP apparatus, plotted as a function of time for PVB coated AA2024-T3 samples in the presence and absence of HT inhibitor pigment. Key: (a) unpigmented PVB, (b) CO_3^{2-} -HT, (c) NO_3^- -HT, and (d) CrO_4^{2-} -HT at pigment volume fractions of 0.2.

1. Pigment preparation

Hydrotalcite (HT) powder ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) was obtained from the Aldrich Chemical Company. Prior to ion exchange, the powder was heat treated at 450°C for 3h, whereupon the layered structure of the hydrotalcite collapses with the evolution of CO_2 and water. 10g of the resultant powder, consisting of an amorphous mixture of magnesium and aluminium hydroxides, was then dispersed in 100 cm^3 of aqueous 0.1 mol dm^{-3} solutions of either NaNO_3 , Na_2CO_3 or Na_2CrO_4 and stirred for 3h. The rehydration of the heat-treated HT leads to the reconstruction of the layered structure, which is accompanied by the intercalation of anions from solution. The two stages of anion exchange process are represented schematically in Figure 1. After anion exchange, the HT powder was exhaustively washed by repeated cycles of centrifugation and re-dispersion in fresh distilled water until sodium ions could no longer be detected in the supernatant when using flame ionisation testing. Finally the powders were allowed to dry in air and pulverised to give a particle size of $<20\mu\text{m}$ diameter.

Details

25

1. Hydrotalcite (HT) powder ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) was calcined at 450°C for 3h, whereupon the layered structure of the hydrotalcite collapsed with the evolution of CO_2 and water. The resultant powder (10g), consisting of an amorphous mixture of magnesium and aluminium hydroxides, was then dispersed in 100 cm^3 of aqueous 0.1 mol dm^{-3} solutions of NaNO_3 and stirred for 3h. The rehydration of the heat-treated

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- HT produced a reconstruction of the layered structure and anion (NO_3^-) incorporation. After anion incorporation, the HT powder was exhaustively washed by repeated cycles of centrifugation and re-dispersion in fresh distilled water until sodium ions could no longer be detected in the supernatant when using a flame emission test.
- 5 Finally the powders were allowed to dry in air and pulverised to give a particle size of $<20\mu\text{m}$ diameter. A polyvinyl butyral (PVB) solution was prepared in ethanol (15% w/w) and sufficient hydrotalcite powder added, in the form of an ethanolic slurry, to give a pigment volume fraction of 0.15 in the final (solvent free) coating. The components were mixed thoroughly using a high shear blender to produce an anti-
- 10 corrosion paint. The hydrotalcite pigmented PVB solution was bar cast on to a clean metal surface and allowed to dry in air. This procedure gave an anti-corrosion coating (paint film) with a dried film thickness of $30\mu\text{m}$ as measured using a micrometer screw gauge.
- 15 2. Hydrotalcite (HT) powder ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) was calcined at 450°C for 3h. The resultant powder (10g), consisting of an amorphous mixture of magnesium and aluminium hydroxides, was then dispersed in 100 cm^3 of aqueous 0.1 mol dm^{-3} solutions of Na_2CO_3 and stirred for 3h. The rehydration of the heat-treated HT produced a reconstruction of the layered structure and anion (CO_3^{2-}) incorporation.
- 20 After anion incorporation, the HT powder was exhaustively washed by repeated cycles of centrifugation and re-dispersion in fresh distilled water until sodium ions could no longer be detected in the supernatant when using a flame emission test. Finally the powders were allowed to dry in air and pulverised to give a particle size of $<20\mu\text{m}$ diameter. A tall-oil modified polyester solution was prepared in 1:1
- 25 ethanol:toluene (15% w/w) and sufficient hydrotalcite powder added, in the form of an ethanolic slurry, to give a pigment volume fraction of 0.2 in the final (solvent free) coating. The components were mixed thoroughly using a high shear blender to produce an anti-corrosion paint. The hydrotalcite pigmented polyester solution was bar cast on to a clean metal surface and allowed to dry in air. This procedure gave an

anti-corrosion coating (paint film) with a dried film thickness of 30 μm as measured using a micrometer screw gauge.

3. Hydrotalcite (HT) powder ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) was calcined at 450°C for
5 3h. The resultant powder (10g), consisting of an amorphous mixture of magnesium
and aluminium hydroxides, was then dispersed in 100 cm^3 of aqueous 0.1 mol dm^{-3}
solutions of ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$) and stirred for 3h. The rehydration
of the heat-treated HT produced a reconstruction of the layered structure and anion
(MoO_4^{2-}) incorporation. After anion incorporation, the HT powder was exhaustively
10 washed by repeated cycles of centrifugation and re-dispersion in fresh distilled water
until ammonia could no longer be detected in the supernatant by alkalisiation and
testing with damp litmus. Finally the powders were allowed to dry in air and
pulverised to give a particle size of $<20\mu\text{m}$ diameter. An ethyl cellulose solution was
prepared in 1:1 ethanol: toluene (15% w/w) and sufficient hydrotalcite powder added,
15 in the form of an ethanolic slurry, to give a pigment volume fraction of 0.15 in the
final (solvent free) coating. The components were mixed thoroughly using a high
shear blender to produce an anti-corrosion paint. The hydrotalcite pigmented ethyl
cellulose solution was bar cast on to a clean metal surface and allowed to dry in air.
This procedure gave an anti-corrosion coating (paint film) with a dried film thickness
20 of 30 μm as measured using a micrometer screw gauge.

2. Sample preparation

All tests were carried out using AA2024-T3 aluminium alloy (composition by weight
25 : 0.5% Si, 0.5% Fe, 3.8 – 4.9% Cu, 0.3 – 0.9% Mn, 1.2 – 1.8% Mg, 0.1% Cr, 0.25%
Zn) supplied by BAE Systems Ltd. Samples were cut into 35 mm square coupons and
abrasively cleaned using an aqueous slurry of 5 μm polishing alumina, followed by
degreasing in acetone. Poly vinyl butyral (PVB) solutions were prepared in ethanol
(15% w/w) and any required amount of exchanged hydrotalcite powder added as an
30 ethanolic slurry. The components were mixed thoroughly using a high shear blender.

Pigmented PVB solutions were bar cast on to the clean sample surface as shown in Figure 2(a) and allowed to dry in air. This procedure gave a dried film thickness of 30 μm as measured using a micrometer screw gauge. Filiform corrosion was initiated by applying a 1 μl volume of aqueous HCl (0.5 mol dm^{-3}) along the length of a 10 mm defect, scribed in the centre of the coated sample using a scalpel blade (see Figure 2(b)). In each case it was ensured that the direction of the scribe was normal to that of substrate extrusion. After allowing any excess water to evaporate, the sample was placed in the environmental chamber of the scanning Kelvin microprobe (SKP) apparatus. Repetitive scans were carried out every 4 hours on a 1 cm^2 area of the coated AA2024-T3 alloy sample encompassing the scribe, using a data point density of 10 points per mm and a mean probe to sample height of 100 microns. In separate experiments, duplicate samples were initiated by the same procedure and placed in a separate environment chamber maintained at a constant relative humidity of 93%. After a period of 1 week following initiation, these samples were removed and photographic images of any corroded regions were recorded.

Full details of the SKP instrument used in this work can be found in reference 3 below. The scanning reference probe consisted of a 125 μm diameter gold wire vibrated along its long axis and normal to the sample surface with amplitude 40 μm and frequency 280Hz. The sample to be scanned was held in a thermostated stainless steel environment chamber. A constant relative humidity of 93% was achieved by the presence of a reservoir containing saturated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (aq), maintained at a temperature of 20°C. Prior to commencement of a scanning experiment, the SKP was calibrated in terms of electrode potential using the established procedure of reference 3. This involved measuring the free corrosion potential, E_{corr} (vs. SCE) and the Kelvin potential, E_{KP} simultaneously for a series of couples (Ag/Ag^+ , Cu/Cu^{2+} , Fe/Fe^{2+} and Zn/Zn^{2+}). For this purpose a series of calibration cells, were prepared by machining wells (8mm diameter, 1mm deep) in discs of the relevant metal (15 mm diameter, 5 mm thick). These wells were then filled with a 0.5 mol dm^{-3} aqueous solution of the respective metal chloride salt (0.5 mol dm^{-3} nitrate salt in the case of Ag). The

influence of the PVB coating on calibration was taken into account by placing a free-standing PVB film in contact with the meniscus of the calibration electrolyte, allowing the electrolyte, PVB film and SKP chamber atmosphere to become equilibrated, and then measuring E_{KP} at the PVB-air interface.

5

Results

3. HT anion exchange capacity

10 The anion exchange properties of both calcined and as-received hydrotalcite was conveniently studied by spectrophotometric means for samples treated with aqueous CrO_4^{2-} solutions. The UV-visible absorbance of the yellow coloured chromate anion at a λ_{max} of 370 nm was used to quantitatively analyse the exchangeable Cr(VI) content of the HT pigments prepared. As-received commercially available HT
15 powder does not readily disperse in aqueous media and a chromate containing 50 vol% ethanol/water was used for this material. Attempts to exchange CrO_4^{2-} into the un-calcined HT matrix proved largely unsuccessful and as a consequence, less than 0.01 mmol of exchangeable Cr(VI) per gram of CrO_4^{2-} -treated starting material could be detected in back exchange experiments employing 0.1 mol dm^{-3} Na_2CO_3 aqueous
20 solutions.

However, following calcination at temperatures of 400°C or higher, treatment of the HT powder with aqueous CrO_4^{2-} containing solutions leads to a significant take-up of Cr(VI) resulting in a yellow colouration of the processed HT powder. An optimum
25 calcination temperature of 450°C , giving maximum anion sorption capacity was used. Back exchange using a 1g quantity of powder dispersed in 100 cm^3 of 0.1 mol dm^{-3} Na_2CO_3 (aq), showed an exchangeable Cr(VI) content of approximately 0.3 mmol/g. Figure 3(a) shows a comparison of Cr(VI) exchange efficiency in the presence of various commonly encountered anions at the same concentration. The effect of
30 successive back exchanges carried out in aqueous carbonate solution for the same 1g

quantity of Cr(VI)-HT is given in Figure 3(b). It may be seen that the majority of ion exchange occurs within the initial back exchange. The total exchange capacity of the Cr(VI)-HT powder, over 4 successive back-exchanges using CO_3^{2-} anions, was calculated to be 0.7 mol equivalents per gram of pigment, corresponding to 0.35 mmol/g of exchangeable CrO_4^{2-} .

4. Anti-corrosion performance of HT pigments

The typical appearance of coated AA2024-T3 samples maintained at 93% rh for a period of 7 days following ffc initiation using aqueous HCl are shown in Figure 4. The marked extent of ffc attack observed for the un-pigmented coating is consistent with results presented previously for the same model system (References 1, 2). However, the three samples illustrated in Figures 4(b), (c) and (d), coated with PVB films incorporating CO_3^{2-} , NO_3^- and CrO_4^{2-} exchanged HT pigments respectively, show markedly reduced susceptibility to ffc attack. The use of image analysis software permits quantification of the sample area affected by ffc activity and the average results obtained for duplicate test samples coated with the four different PVB based films are summarised in Figure 5. Further details of parameters such as the average number of filaments per sample are average filament extension and width is provided in Table 1. Although the presence of exchangeable nitrate ions appear to more efficiently inhibit ffc when compared to carbonate and a corroded sample area basis, there are a significantly greater number of what appear to be filament initiation sites. NO_3^- ions appear to markedly limit the size of filaments, though not their number, while the presence of CO_3^{2-} acts in the reverse fashion, limiting the number, though not the size of any filaments. As expected, the incorporation of chromate ions profoundly inhibits any ffc activity, and the anti-corrosion performance of the Cr(VI)-HT pigment is comparable with SrCrO_4 under the same conditions. However, it should be noted that the actual CrO_4^{2-} content of the HT pigment coating, calculated on a molar basis, is about 30 times less than for the same polymer system containing SrCrO_4 at similar pigment volume fractions. Obviously this has important

environmental connotations with regard to the long term release of Cr(VI) species from anti-corrosion coatings based on these materials.

5. SKP analysis of pigment efficiency

5 Repeated scanning of AA2024-T3 samples coated with unpigmented PVB films and with PVB films containing the 3 different types of HT based pigments at a fixed volume fraction of 0.2, was used to generate a series of time lapse animations showing dynamic changes in local free corrosion potential (E_{corr}). A methodology for
10 quantifying the time-dependent progress of ffc filament populations by comparing the spatial distribution of E_{corr} values between successive SKP scans has been described in detail in references 22 and 23. Using this approach, the effect of HT pigmentation on ffc delamination kinetics is shown in figure 6. The advantage of using the SKP technique to quantify delaminated area in terms of E_{corr} , in preference to visual
15 inspection methods, is that some areas of underfilm corrosion may be obscured by the inclusion of pigment. It may be seen from Figure 6 that for an unpigmented PVB coating the ffc delaminated area growth is linear with respect to time. However, for each HT pigment type, an initial increase of delaminated area with time over the first 24 h after initiation, is followed by a marked reduction in delaminated area growth for
20 further periods of up to 4 days. As observed previously in Figures 4 and 5, the SKP analysis confirms that the efficiency of ffc inhibition increases with the type of exchangeable anion in the order $\text{CO}_3^{2-} < \text{NO}_3^- < \text{CrO}_4^{2-}$. The potential mode of operation of an anion exchanged HT inhibitor pigment on a corroding aluminium surface is thought to proceed in two stages. The first involves the initial removal of
25 Cl^- ions at the initiation stage and the subsequent release of inhibitor ions into the electrolyte covered bare metal defect. The second mode of inhibition occurs in the underfilm region when the initiating electrolyte has penetrated the metal-coating interface. Upon contact with the chloride-containing electrolyte within a filament head, inhibitor anions are released directly into the head regions, along with
30 concomitant removal of Cl^- from the underfilm electrolyte.

Conclusion

- The examples studied the efficiency of carbonate, nitrate and chromate exchanged HT pigments in forestalling filiform corrosion on PVB coated AA2024-T3 aluminium alloy surfaces by a combination of scanning Kelvin probe (SKP) and visual examination techniques. Samples were initiated by placing a known quantity of aqueous HCl on to a penetrative coating defect and maintained at a constant relative humidity of 93% for periods of up to 1 week.
- As can be seen the incorporation of the HT based pigments profoundly inhibits the progress of ffc activity for up to 7 days following initiation. SKP quantification of the growth of delaminated area with time reveals that for each inhibitor ion, an initial increase in delaminated area over an initial 24h period is followed by a marked slow-down in rate for the remaining experimental duration. The efficiency of the inhibition of ffc is dependent upon the nature of the exchangeable anion present and increases in the order $\text{CO}_3^{2-} < \text{NO}_3^- < \text{CrO}_4^{2-}$.

Table 1: Characteristics of ffc behaviour observed for PVB coated AA2024-T3 samples in the presence and absence of HT inhibitor pigments.

Inhibitor	Average filament extension (mm)	Average filament width (mm)	Number of filaments	Corroded area (mm ²)
none	2.92	0.93	10	35.32
carbonate	1.63	0.8	4	7.95
nitrate	0.68	0.52	12	4.66
chromate	0.9	0.71	1	1.45

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Claims

1. An anti-corrosion formulation comprising an inhibitor pigment dispersed in a carrier characterised in that the inhibitor pigment is an exchangeable anion-bearing hydrotalcite.
5
2. An anti-corrosion formulation as claimed in claim 1 in which the carrier is a film-forming formulation or binder.
- 10 3. An anti-corrosion formulation as claimed in claim 2 in which the film-forming formulation or binder is a polymeric binder.
4. An anti-corrosion formulation as claimed in claim 2 or 3 in which the binder is a polyvinyl butyral (PVB) film or a tall-oil modified polyester solution.
15
5. An anti-corrosion formulation as claimed in any one of claims 1 to 4 in which the carrier is a primer or paint or can form a lamellar coating.
6. An anti-corrosion formulation as claimed in any one of claims 1 to 5 in which the hydrotalcite is a lamellar mixed hydroxide represented by the general formula $[M^{2+}_{1-x} M^{3+}_x(OH)_2]^{x+} [A^{x-} \cdot nH_2O]$, where M2 is a divalent metal, M3 is a trivalent metal and A is an exchangeable anion.
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7. An anti-corrosion formulation as claimed in claim 5 or 6 in which M2 is magnesium and M3 is aluminium.
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8. An anti-corrosion formulation as claimed in any one of claims 5 to 7 in which the exchangeable anion is an anion with corrosion inhibitor properties.

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9. An anti-corrosion formulation as claimed in any one of claims 5 to 8 in which the exchangeable anion is an oxidising agent.
10. An anti-corrosion formulation as claimed in any one of claims 5 to 8 in which the exchangeable anion is a base.
11. An anti-corrosion formulation as claimed in any one of claims 5 to 10 in which the exchangeable anion is capable of becoming strongly adsorbed at metal surfaces and (hydr)oxide covered metal surfaces.
12. An anti-corrosion formulation as claimed in any one of claims 5 to 10 in which the exchangeable anion is capable of forming sparingly soluble precipitates with metal cations.
13. An anti-corrosion formulation as claimed in any one of claims 5 to 12 in which the anion is a transition metal oxyanion, a group (III) oxyanion, a group (IV) oxyanion, a group (V) oxyanion, a group (VI) oxyanion or a group (VII) oxyanion.
14. An anti-corrosion formulation as claimed in claim 13 in which the anion is nitrate (NO_3^-), nitrite (NO_2^-), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), molybdate (MoO_4^{2-}) or permanganate (MnO_4^{2-}).
15. An anti-corrosion formulation as claimed in any one of claims 5 to 14 in which the formulation is made by a process comprising (i) heating the hydrotalcite clay and (ii) re-hydrating the clay in an aqueous solution containing the anion.
16. An anti-corrosion formulation as claimed in claim 15 in which the hydrotalcite is a magnesium aluminium hydroxy-carbonate powder.

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17. An anti-corrosion formulation as claimed in claim 16 in which the hydrotalcite is $(\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O})$.
18. An anti-corrosion formulation as claimed in any one of claims 15 to 17 in which the hydrotalcite clay is calcined at a temperature of between 200°C and 600°C to produce an amorphous mixture of Al and Mg hydroxides and the amorphous mixture of hydroxides is then cooled to room temperature and rehydrated using an aqueous solution containing the exchangeable anion.
19. A method of treating a metal surface with an anticorrosion pigment which method comprises contacting the surface with a formulation as claimed in any one of claims 1 to 18.
20. An anti-corrosion pigment which comprises an exchangeable anion-bearing hydrotalcite.
21. An anti-corrosion pigment as claimed in claim 20 in which the hydrotalcite is a lamellar mixed hydroxide represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{x-} \cdot n\text{H}_2\text{O}]$, where M2 is a divalent metal, M3 is a trivalent metal and A is an exchangeable anion.
22. An anti-corrosion pigment as claimed in claim 20 or 21 in which M2 is magnesium and M3 is aluminium.
23. An anti-corrosion pigment as claimed in any one of claims 20 to 22 in which the exchangeable anion is an anion with corrosion inhibitor properties.
24. An anti-corrosion pigment as claimed in any one of claims 20 to 23 in which the exchangeable anion is an oxidising agent.

25. An anti-corrosion pigment as claimed in any one of claims 20 to 24 in which the exchangeable anion is a base.
- 5 26. An anti-corrosion pigment as claimed in any one of claims 20 to 25 in which the exchangeable anion is capable of becoming strongly adsorbed at metal surfaces and (hydr)oxide covered metal surfaces.
- 10 27. An anti-corrosion pigment as claimed in any one of claims 20 to 26 in which the exchangeable anion is capable of forming sparingly soluble precipitates with metal cations.
- 15 28. An anti-corrosion pigment as claimed in any one of claims 20 to 22 in which the anion is a transition metal oxyanion, a group (III) oxyanion, a group (IV) oxyanion, a group (V) oxyanion, a group (VI) oxyanion or a group (VII) oxyanion.
- 20 29. An anti-corrosion pigment as claimed in claim 28 in which the anion is nitrate (NO_3^-), nitrite (NO_2^-), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), molybdate (MoO_4^{2-}) or permanganate (MnO_4^{2-}).
- 25 30. An anti-corrosion pigment as claimed in any one of claims 20 to 29 in which the pigment is made by a process comprising (i) heating the hydrotalcite clay and (ii) re-hydrating the clay in an aqueous solution containing the anion.
- 30 31. An anti-corrosion pigment as claimed in claim 30 in which the hydrotalcite is a magnesium aluminium hydroxy-carbonate powder.
32. An anti-corrosion pigment as claimed in claim 31 in which the hydrotalcite is $(\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O})$.

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33. An anti-corrosion pigment as claimed in any one of claims 30 to 32 in which the hydrotalcite clay is calcined at a temperature of between 200⁰C and 600⁰C to produce an amorphous mixture of Al and Mg hydroxides and the amorphous mixture of hydroxides then cooled to room temperature and rehydrated using an aqueous solution containing the exchangeable anion.
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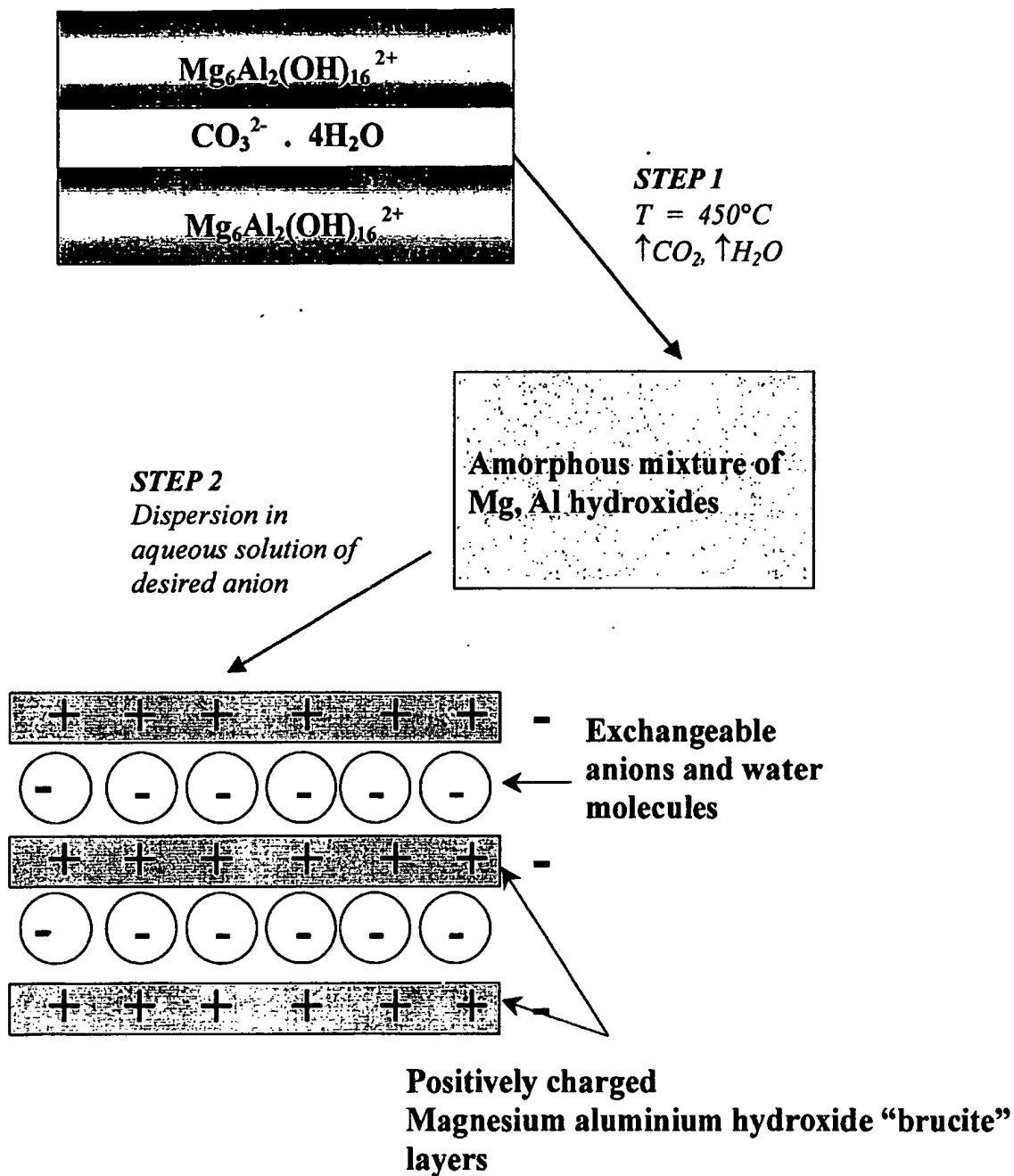


Fig. 1

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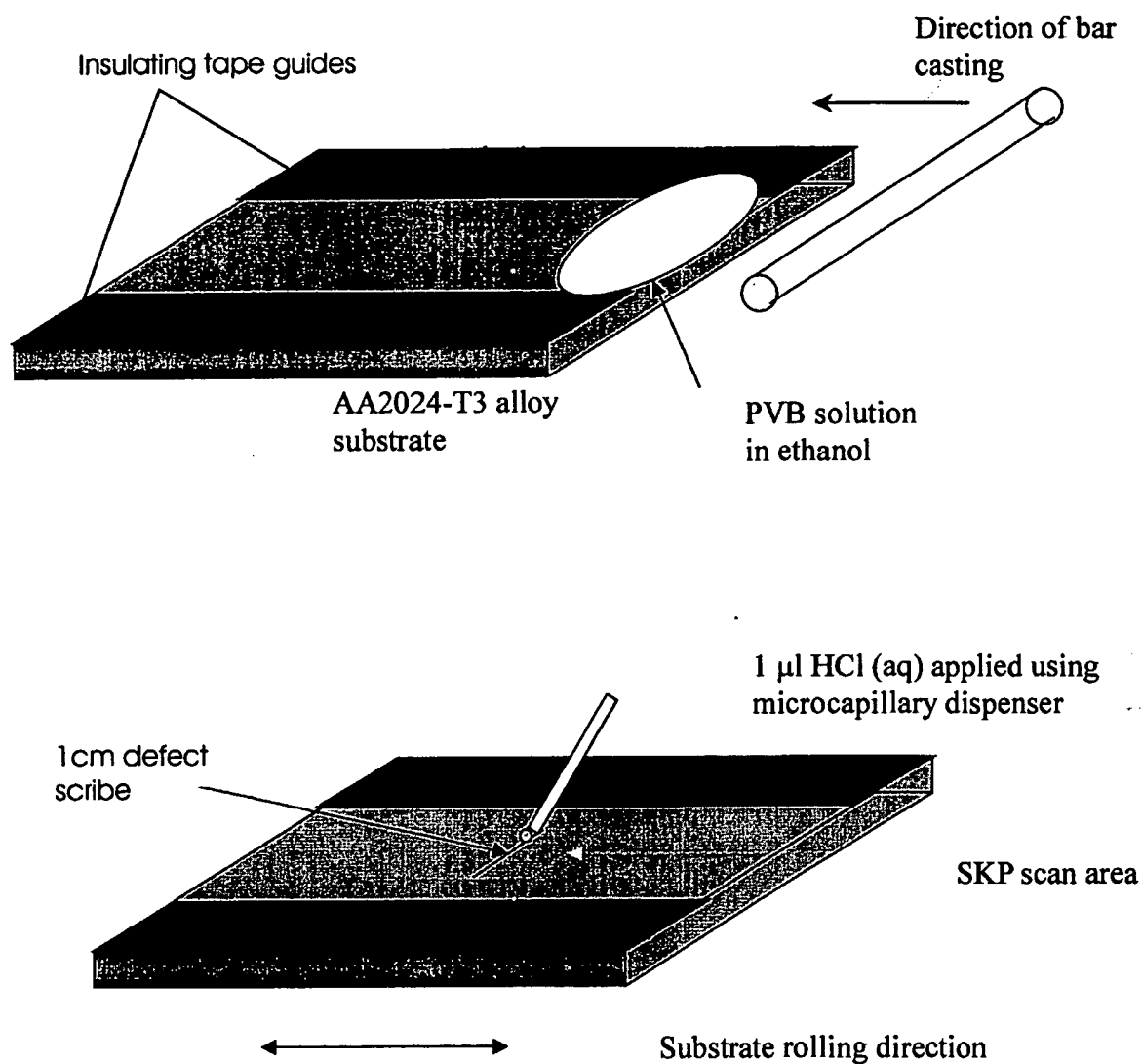


Fig. 2

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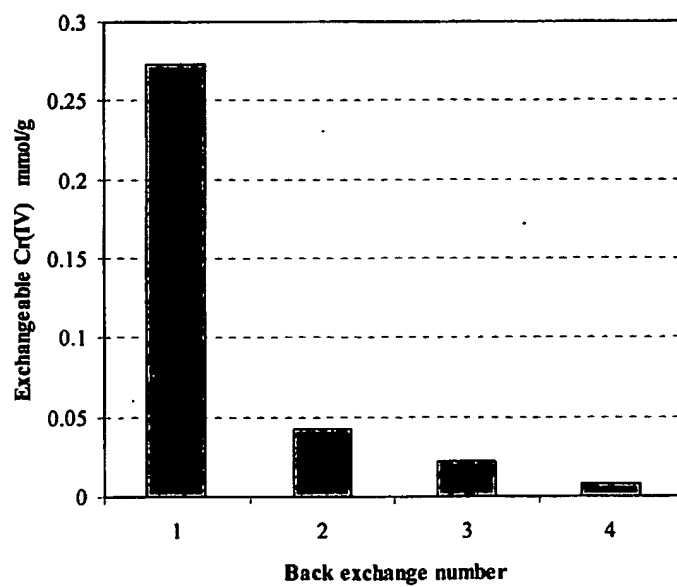
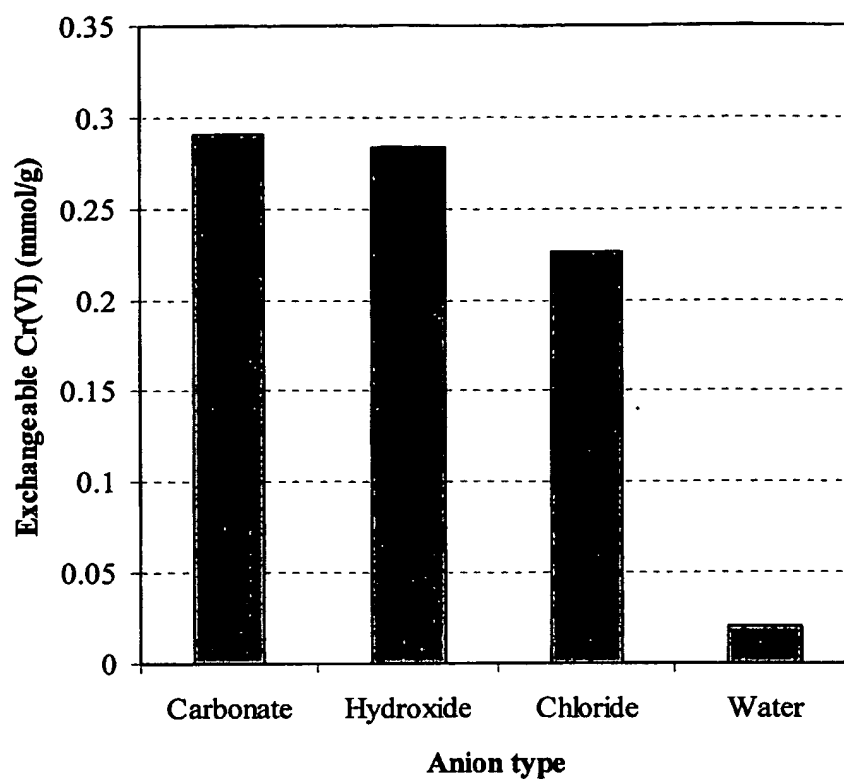


Fig. 3

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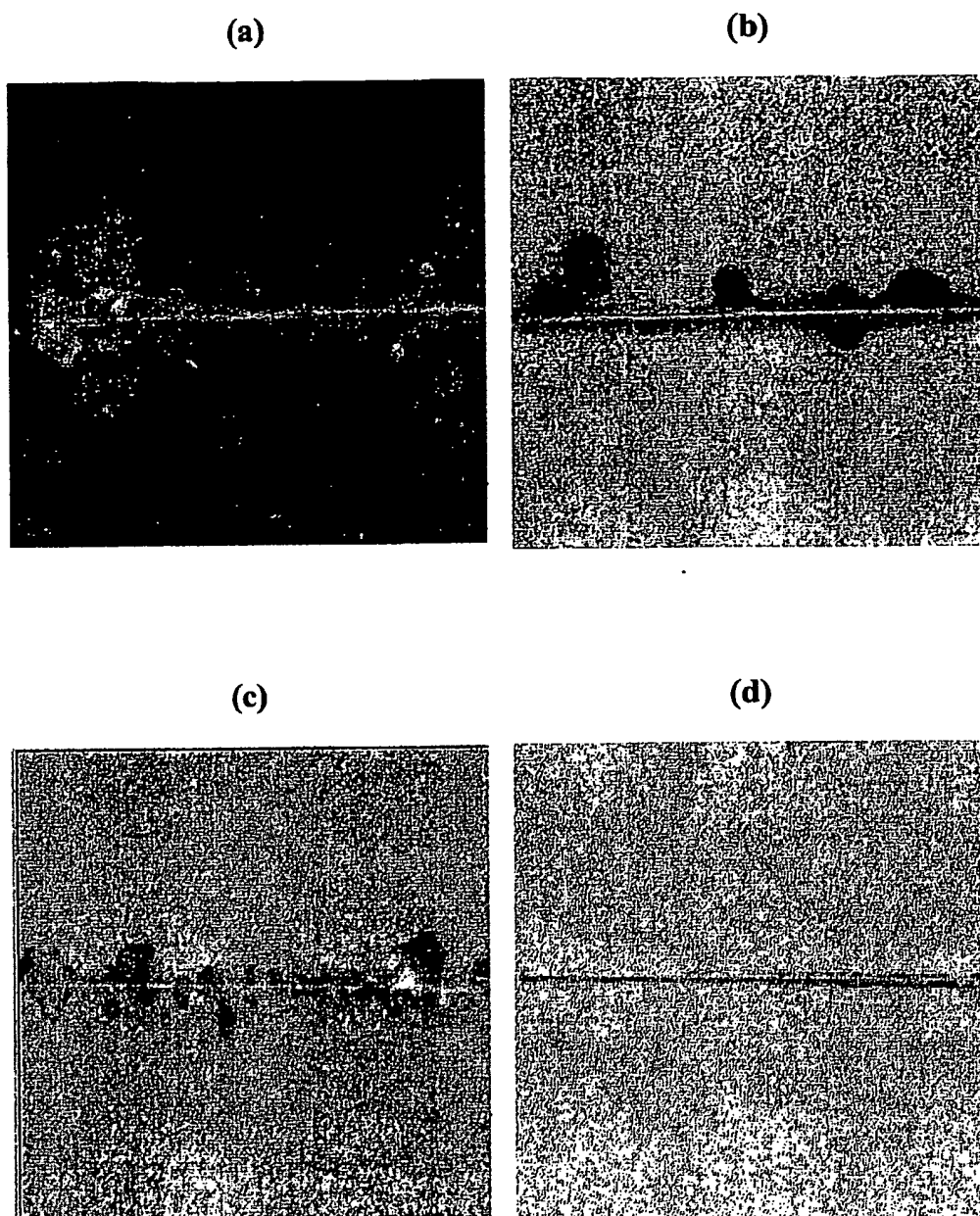


Fig. 4

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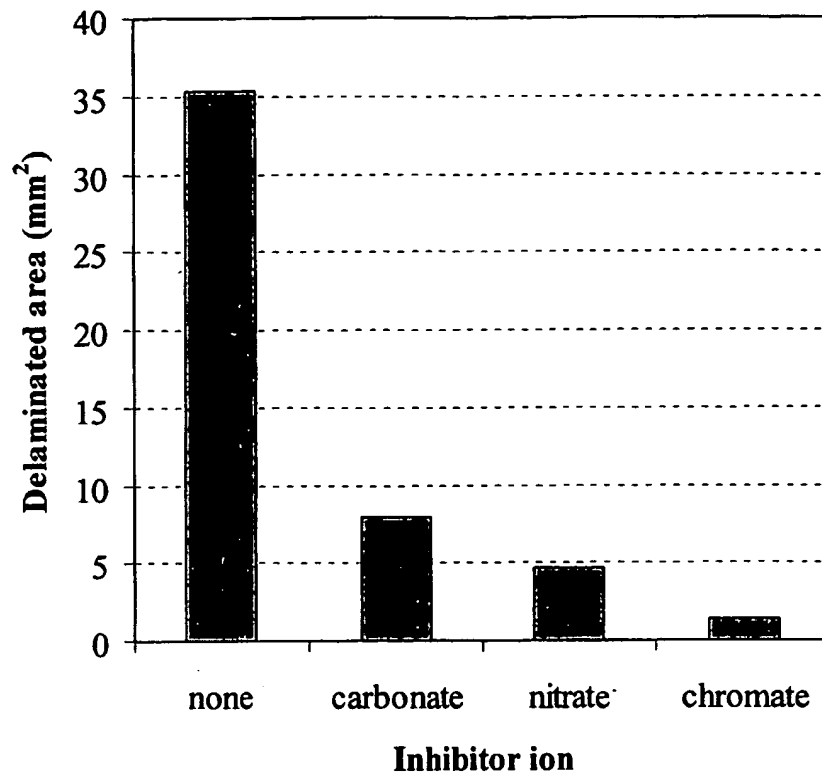


Fig. 5

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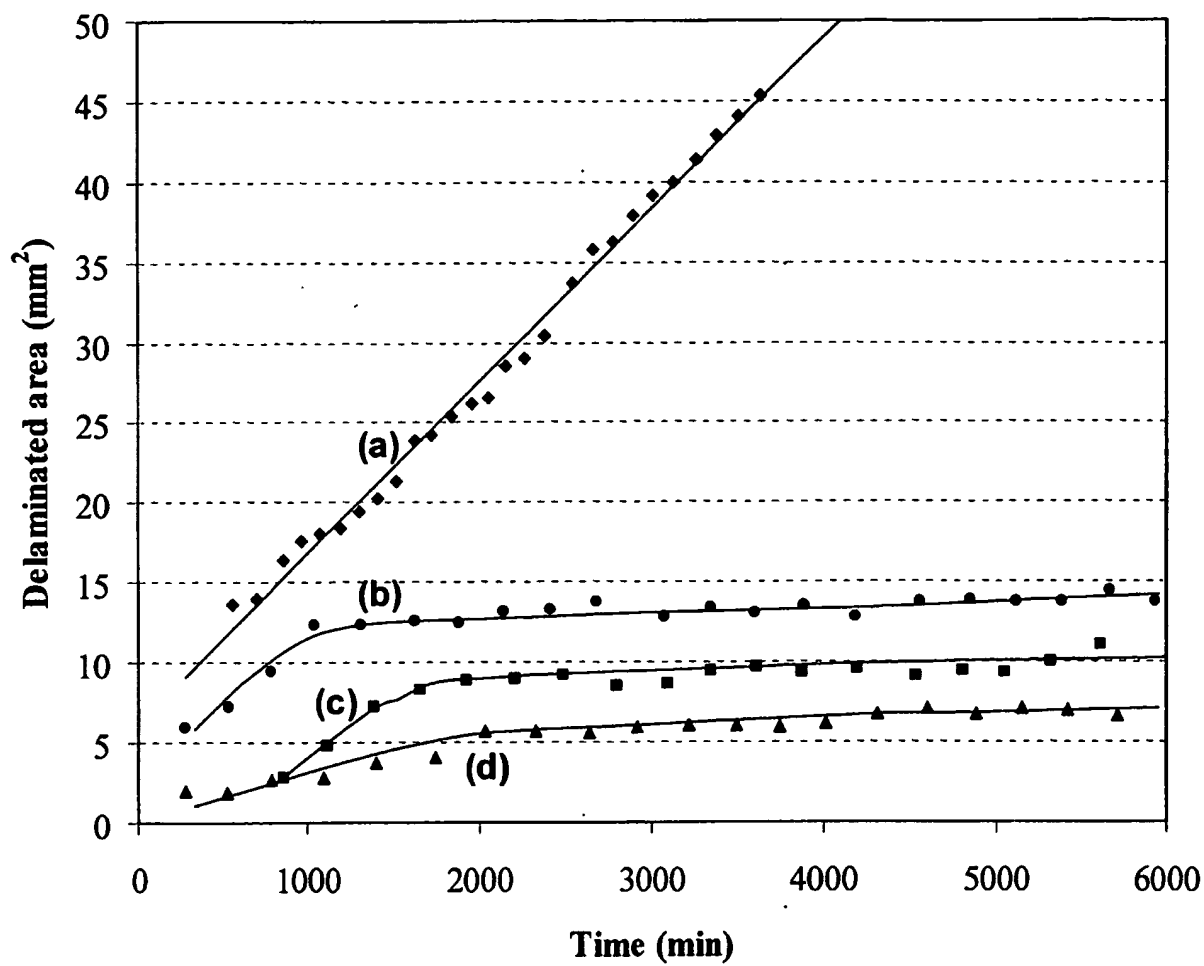


Fig. 6

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